

AD No. 14 971
ASTIA FILE COPY

(+) α -PHENETHYL CHLORIDE AND (-)-2-PHENYLPENTANE

By Robert L. Burwell, Jr. and Alfred D. Shields

Technical Report No. 6

to

THE OFFICE OF NAVAL RESEARCH

Project Number NR 055-199

Contract N7 onr-54006

at

Northwestern University

under the direction of Robert L. Burwell, Jr.

August 1, 1953

ABSTRACT

In the course of the preparation of optically active 2-phenylpentane (the action of strong acids upon which is under investigation) certain stereochemical data of general interest have been developed. Our results permit the assigning of limits to the rotation of the important material, α -phenethyl chloride. The rotation of the optically pure material lies between 109° and 133° . The lower limit results from the conversion of α -phenethyl alcohol to the chloride. The upper limit results from the conversion of the chloride to 4-phenyl-1-pentene via reaction with sodium allyl. The pentene is hydrogenated to 2-phenylpentane the rotation of which is known in the optically pure form.

The only previously reported method of preparing α -phenethyl chloride of high rotation gives poor yields. This method, due to Gerrard, involves the action of phosphorus oxychloride on α -phenethyl alcohol in the presence of pyridine. The addition of pyridine hydrochloride is now found to give much improved yields with but slight loss in optical purity.

This note describes experiments which place upper and lower limits upon the rotation of optically active α -phenethyl chloride via conversion of α -phenethyl alcohol to the chloride and via conversion of the chloride to 2-phenylpentane. It also describes a preparation of α -phenethyl chloride of high rotation in much improved yield.

Gerrard² has described a preparation of the chloride employing

(2) W. Gerrard, J. Chem. Soc., 110 (1945).

pyridine and phosphorus oxychloride which gives much larger rotations than methods previously employed. We have confirmed these results and obtained a chloride the rotation of which very slightly exceeded the highest reported by Gerrard. This establishes a lower limit to α_D^{25} of 109°.

Employing the Letsinger³ modification of the Wurtz reaction,

(3) R.L. Letsinger, J. Am. Chem. Soc., 70, 406 (1948).

optically active α -phenethyl chloride was converted to 4-phenyl-1-pentene by reaction with allyl sodium. This was hydrogenated to 2-phenylpentane. From the ratio of the observed rotation of this material to that reported for the optically pure material by Cram,⁴

(4) D.J. Cram, ibid., 74, 2152 (1952).

the upper limit to the rotation of α -phenethyl chloride is 133°. No assignment can be made of the difference between 109° and 133° as to loss of optical purity in forming the chloride from the alcohol and in forming the olefin from the chloride. It is unlikely that any significant racemization accompanies the hydrogenation of the

olefin with platinum oxide.^{5,6}

(5) G.S. Gordon III and R.L. Burwell, Jr., *ibid.*, 71, 2355 (1949).

(6) D.J. Cram, *ibid.*, 74, 5518 (1952). In Cram's 3-phenyl-1-butene, the double bond is one carbon atom nearer the optical center.

Dr. E.L. Eliel has pointed out to us that one may compute an upper limit to the rotation of the chloride from the rotation of the ether of α -phenethyl alcohol⁷ and from the formation⁸ of this

(7) K. Mislow, *ibid.*, 73, 4043 (1951).

(8) E.D. Hughes, C.K. Ingold and A.D. Scott, *J. Chem. Soc.*, 1201 (1937). See also W. Gerrard and M.F. Lappert, *ibid.*, 1024 (1951).

ether from optically active chloride. This value is 129° which is probably within the experimental uncertainty of both procedures.

Although Gerrard's preparation of α -phenethyl chloride gives material of high rotation, yields are but about 40%. The rest of the carbinol apparently remains as a phosphoric ester. Extending the reaction time to three weeks does not improve yields. At the completion of the phosphorus oxychloride addition, the reaction mixture is a white viscous mass. Addition of pentane did not affect this or improve yields. A mixture prepared from carbinol (0.125 mole), phosphorus oxychloride (0.125 mole), pyridine (0.375 mole) and chloroform (150 cc.) remained liquid and gave a yield of crude chloride of 70%. On the view that the reaction, as ordinarily run, was limited by unavailability of chloride ion to react with phosphoric esters, a mixture similar to the one above was prepared with the addition of pyridine hydrochloride (0.75 mole per mole of pyridine). Yields of crude chloride of 82% and of purified chloride of 70% were obtained. The rotations are but 86% of those obtained by the unmodified pro-

cedure of Gerrard but for many applications the increased yield will make the procedure advantageous.

Experimental

All rotations are homogeneous and given for 1 dm.

For optically pure phenylmethylcarbinol, $\alpha_D^{25} +43.7^\circ$.

- (9) A. McKenzie and G.W. Clough, J. Chem. Soc., 103, 687 (1913).
 E. Downer and J. Kenyon, ibid., 1156 (1939). $d\alpha/dt$ may be
 obtained from R.H. Pickard and J. Kenyon, ibid., 99, 45 (1911).

Preparation of α -phenethylchloride.- 0.466 mole of phosphorus oxychloride was added to a solution of 1.40 mole pyridine and 0.466 mole phenylmethylcarbinol, $\alpha_D^{25} - 38.93^\circ$, in 300 cc. of pentane with the temperature maintained at -10° to 0° during the addition. After sixteen hours at 5° followed by twenty four at 25° , the reaction mixture was decomposed with ice and extracted with ether. After washing, the ether extract was evaporated and pentane added. This solution was washed with three portions of 85% phosphoric acid and then with water. It was dried with potassium carbonate and distilled at 17 mm., b.p. $78-82^\circ$ (uncorr.), yield, 43%, $\alpha_D^{25} +97.4$. Correcting to optically pure starting material, $\alpha_D^{25} +109^\circ$.

The procedure of improved yields follows: 0.463 mole of hydrogen chloride gas was passed into a solution of 1.07 mole pyridine and 0.204 mole phenylmethylcarbinol, $\alpha_D^{25} +10.95$, in 200 cc. chloroform, with the reaction mixture kept at -15° . 0.204 mole phosphorus oxychloride was added with the solution at about the same temperature. After a day at room temperatures, it was decomposed with ice. The chloroform layer was extracted with 85% phosphoric acid, washed, dried and distilled at 8 mm.; b.p. 68° ; yield,

-4-

70%; α_D^{25} -23.65° or corrected to optically pure carbinol, -24° .

4-Phenyl-1-pentene.— This was prepared by action of sodium allyl on α -phenethylchloride following the preparation of 4-methyl-1-decene by Letsinger and Traynham¹⁰ save that the octane was not

(10) R.L. Letsinger and J.G. Traynham, J. Am. Chem. Soc., 70, 3342 (1948).

replaced by hexane and the chloride was added at -45° to -20° . The phenylpentene was fractionated in a small Stedman column: b.p. $187-188^\circ$ (uncorr.); n_D^{25} 1.5020; yields, about 80%. From three experiments, the value of the ratio of the rotation of pentene to chloride is best taken as 0.121. The sign of rotation and presumably the configuration is inverted.

A similar experiment in which allyl magnesium bromide replaced sodium allyl gave a pentene whose rotation was but 43% of that with the sodium allyl.

2-Phenylpentane was obtained by hydrogenating the olefin in alcoholic solution with Adams' platinum oxide at room temperatures. The material was chromatographed on silica gel and fractionated, n_D^{25} 1.4856. From Cram's⁴ value for the pentane, α_D^{25} 15.00° , using our measurement of temperature coefficient, α_D^{25} 14.91° . Whence, from the best values of our experiments, α_D^{25} 16.1° for the optically pure pentene and of like sign to the pentane.

Department of Chemistry
Northwestern University
Evanston, Illinois